Optics and Laser Technology 105 (2018) 249–256

Contents lists available at ScienceDirect

Optics and Laser Technology

journal homepage: www.elsevier.com/locate/optlastec

Full length article

Systematic discussions on structural, optical, mechanical, electrical and its application to NLO devices of a novel semi-organic single crystal: Guanidinium tetrafluoroborate (GFB)

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ARTICLE INFO

Article history:
Received 4 October 2017
Received in revised form 8 December 2017
Accepted 9 March 2018

Keywords:
Non-centrosymmetric
Rocking curve
Urbach energy
Piezoelectric
Non-linear optical crystal

ABSTRACT

A new novel semi-organic crystal guanidinium tetrafluoroborate (GFB) was grown by slow evaporation solution growth technique. The cell parameters and its crystalline nature were determined from powder X-ray diffraction analysis. The strain of the material was found using Hall-Williamson plot. The high resolution X-ray diffraction study reveals the crystalline perfection of the grown crystal. The functional groups were confirmed through Fourier transform infrared spectral analysis. The UV–vis-NIR study shows that the crystal is transparent in the entire visible region and other optical constants were also calculated. The Vicker's hardness study shows that the crystal exhibits reverse indentation size effect. The dielectric property was analysed for different temperatures and frequencies. Piezoelectricity was confirmed by determining the piezoelectric charge coefficient. The second harmonic generation of the grown crystal was determined using Kurtz-powder technique and compared with that of KDP crystal. The thermal stability of the crystal was found using TG-DTA analyses.

1. Introduction

In recent years, nonlinear optical (NLO) crystals have emerged to be one of the most attractive fields of current interest in view of their vital applications in areas like optical modulation, optical switching, frequency switching and optical data storage for the developing technologies in telecommunication and in efficient signal processing [1]. In nonlinear optics, organic materials have advantages such as large NLO coefficients and structural diversity or flexibility. However, organic NLO crystals are having certain disadvantages such as low mechanical and thermal stabilities. In turn, inorganic materials possess advantages, such as good physiochemical stability and good mechanical strength but they exhibit some disadvantages like low NLO coefficients, structural inflexibility [2]. Hence, in order to overcome these disadvantages, a new class of materials called semi-organic materials were developed [3].

This leads to world-wide attempts to explore suitable semi-organic systems which overcome the limitation on the maximum attainable nonlinearity in inorganic materials and the moderate success in growing device-grade single crystals in organic materials [4]. Semi-organics include organic-inorganic salts and metal-organic coordination compounds [5]. In semi-organics, polarisable organic materials are stoichiometrically bound within an inorganic host. These results in the materials having high polarisability, high thermal stability and high mechanical stability.

Guanidine is a strong base which readily reacts with all types of acids to give salts with good crystallinity. The presence of size potential 13 donor sites for hydrogen bonding interactions and delocalized electron systems have made guanidine compounds, potentially interesting material for NLO applications. Organic guanidine carbonate material has enhanced NLO efficiency compared to KDP. This result in the formation of guanidinium species useful for designing molecular complexes with exactly planned chemical and physical properties suitable for non-linear optics [6]. The introduction of halogen group (fluorine) into boron, results in a good NLO behaviour which in turn increases the interest towards it [7]. In the present work, a strong base, guanidine carbonate gets reacted with an inorganic acid, tetrafluoroboric acid to yield guanidinium tetrafluorborate (GFB). The fluoroboric acid has an active hydrogen donor group which readily gives its ion to the guanidine atom and turns into an anion, similarly the extra ion gained by the guanidine turns into guanidinium cation. In the present work the structural, optical, thermal, mechanical, piezoelectric and NLO property of the guanidinium tetrafluoroborate crystal is discussed in detail.

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https://doi.org/10.1016/j.optlastec.2018.03.006
0030-3992/

2. Experimental

2.1. Synthesis and crystal growth

The GFB crystal was synthesised from a high purity grade guanidine carbonate and tetrafluoroboric acid in an equimolar ratio 1:1. The calculated amounts of salts were dissolved in the double-distilled water. In order to attain homogenous concentration and temperature throughout the entire solution, it was stirred well for 6 h. The saturated solution was then filtered and kept for crystallization process under room temperature by slow evaporation technique. Transparent colourless crystal of dimension $8 \times 7 \times 5$ mm^3 was harvested in a period of 20 days is shown in the Fig. 1. The synthesized salt was purified by repeated recrystallization process in deionised water. The reaction scheme is given in Fig. 2,

$$\underset{\text{Guanidine carbonate}}{C_2H_7N_3O_3} + \underset{\text{tetrafluoroboric acid}}{HBF_4} \rightarrow \underset{\text{Guanidinium tetrafluoroborate}}{CH_6BF_4N_3} + H_2 + CO_3$$

The amino groups present in the base cation $(NH_3)^+$ are protonated and thus counterbalance the negative charge in the tetrafluoroborate $(BF_4)^-$ ion.

3. Characterizations

The powder X-ray diffraction study was carried out using XPERT diffractrometer with Cu-kα (λ = 1.5405 Å) radiation. The high resolution X-ray diffraction study was carried out using PANanlytical X-Pert Pro MRD resolution 0.0001°/0.36 arcsec Ge-(220) monochromator triple axis (Xe) detector pixel detector. The FT-IR spectrum was recorded using Cary spectrophotometer between the range 4000–400 cm^{-1}. The UV-vis-NIR spectrum was analysed using LABINDIA model UV 3092 spectrophotometer. The dielectric study was performed using HOIKI 3532-50 LCR HITESTER detector. The second harmonic generation was detected using Kurtz and Perry powder technique. Microhardness analysis was carried out using a Shimadzu microhardness tester with a diamond indenter. The thermo gravimetric analysis (TG) and differential thermal analysis (DTA) were performed using Perkin Elmer diamond TG-DTA thermal analyzer.

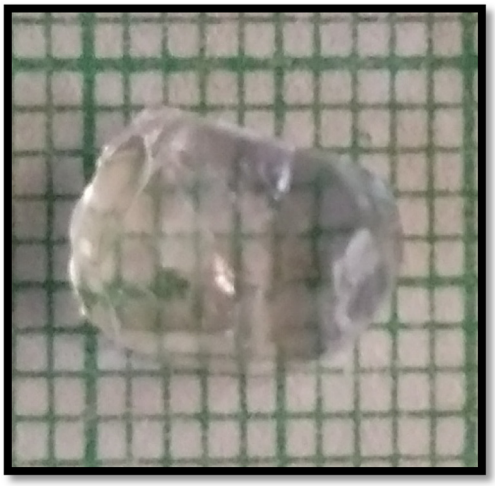

Fig. 1. As grown GFB single crystal.

4. Results and discussion

4.1. X-ray diffraction analysis

The single crystal X-ray diffraction study was carried out for the grown crystal. It belongs to rhombohedral crystal system with space group R3m. The grown GFB crystal was crushed finely and subjected to powder X-ray diffraction study. The sample was scanned over the range of 10°–80° at a scan rate of 5°/min and the indexed X-ray diffraction graph is shown in the Fig. 3. The obtained cell parameters are, a = b = 7.38 Å and c = 8.99 Å with α = β = 90°, γ = 120°.This shows a good agreement with the reported values as given in the Table 1.

The Hall-Williamson equation was used to reveal the strain in the lattice of grown crystal with the help of the Eq. (1),

$$\beta \cos\theta = \frac{k\lambda}{\tau} + \eta \sin\theta \quad (1)$$

where β, θ, k, λ and τ are full width at half maxima (FWHM) of diffraction peak, Bragg diffraction angle of the peak, Scherrer's constant, wavelength of X-rays and crystallite size respectively. The graph was plotted between sin θ and β cos θ as shown in the Fig. 4. The slope of the graph gives the value of strain. The value of strain (η) was found to be −0.06101. In general, the negative value of the strain reveals the existence of vacancy type of defects in the crystal [8].

4.2. High resolution X-ray diffraction analysis

The high resolution diffraction curve (DC) was recorded for the grown single crystal by employing the multicrystal X-ray diffractometer with MoKα_1 radiation. The diffraction curve (DC) is shown in the Fig. 5. The DC exhibits a single peak, which indicates that the specimen is free from structural grain boundaries. The FWHM full width at half maximum (FWHM) is 89 arc sec. The value is more than that of the expected value from the plane wave theory of the dynamical X-ray diffraction for an ideally perfect crystal, but it is close to that expected for nearly perfect real crystals. In general, the broadening of rocking curve without any splitting in the cure and low level asymmetry with respect to the peak position could be attributed to the defects, like mosaic blocks, dislocation, Frenkel defects, implantation induced defects (due to simultaneous existence of vacancies as well as interstitial defects), etc. These kinds of defects are very commonly observed in almost all real crystals, both man made crystals and grown by natural geological processes. The slight asymmetry is seen in the DC and through which one can expect the predominant occupation of vacancy or interstitial defects [9]. From the DC, we could see that the scattering intensity is slightly higher in the negative direction than in the

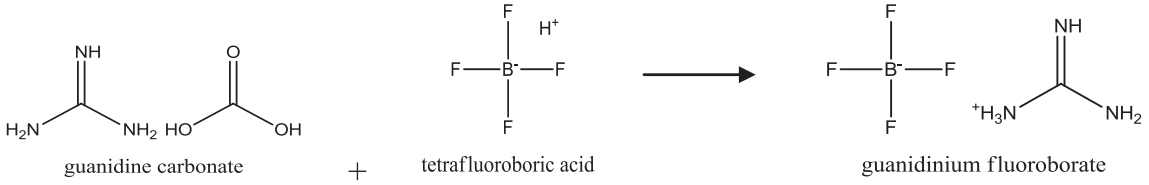

Fig. 2. Reaction scheme of GFB compound.